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Investigations into the conversion of ethanol to 1,3-butadiene using $MgO:SiO_2$ supported catalysts

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Abstract:

We report the applicability of ZrO_2/ZnO impregnated onto a variety of $MgO:SiO_2$ materials as heterogeneous catalysts for the conversion of ethanol to 1,3-butadiene. The selectivity to 1,3-butadiene is affected by the ratio of the basic MgO to the acidic SiO_2, with higher selectivities being observed as the mole fraction of MgO increases. The catalysts have been characterised by SEM, XPS, pXRD, BET surface area measurements and ^{29}Si solid-state NMR spectroscopy.

Keywords:

Heterogeneous catalysts, ethanol, 1,3-butadiene, supported catalysts

1. Introduction:

A main challenge facing the bulk chemical industry in the 21st Century is the security and sustainability of its supply chains. This is highlighted by recent issues in the cost and provision of 1,3-butadiene (1,3-BD). 1,3-BD is typically isolated from fractions resulting from the steam cracking of naphtha, with the 1,3-BD being separated after distillation and extractive distillation processes.[1] 1,3-BD is a by-product of this process – the desired product being ethene. With the increasing cost of oil and the desire for lighter hydrocarbons the production of 1,3-BD has decreased, and thus its market price has increased. This is further compounded by the increased volume of "shale gas" being produced.[2] This typically contains ethane (*ca.* 10 %) which can be dehydrogenated becoming a competitive, 1,3-BD free, source of ethene. This reduces the amount of ethene required by the cracking process and thus reducing the supply of 1,3-BD. However, neither of these processes are sustainable in the long term.[3] There is a desire to produce 1,3-BD from a sustainable source, one such process being explored is the production from ethanol. This is by no means a new process, it has been known since the early part of the 20th Century.[4] The mechanism is thought to be as follows: 1) ethanol is dehydrogenated to acetaldehyde; 2) two molecules of acetaldehyde combine to form acetaldol; 3) this is then dehydrated to from crotonaldehyde; 4) followed by a Meerwein-Ponndorf-Verely (MVP) reduction to generate crotyl alcohol with a subsequent dehydration to generate 1,3-BD.[5] By-products of this process have been shown to be ethene, diethyl ether, ethyl acetate, acetone, butenes and butan-1-ol to name but a few.

There are several reported systems that are active for the catalytic conversion of ethanol to 1,3-BD.[6-17,4,5,18-22] One of the present authors has shown that a Zn(II)/Zr(IV)/SiO_2 system is effective, with selectivities upto 48 % being achieved (although these could be increased with the addition of acetaldehyde in the feed).[6] Ohnishi *et al* have prepared a series of MgO:SiO_2 (1:1 ratio) catalysts and claimed a conversion of 50 % and selectivity of 84 % towards 1,3-BD (WHSV = 0.15 h^{-1}, T = 350 ºC).[10] However, Niiyama using MgO:SiO_2 achieved yields in the region of 30-40 %.[9] With simple MgO:SiO_2 Kvisle achieved a selectivity to 1,3-BD of

approximately 30 % (WHSV = 0.03 h^{-1}, T = 350 ºC), this could be increased with added acetaldehyde.[8]

In all cases the materials are simply prepared (a pre-requisite for large-scale applications) by simple incipient wetness procedures from MgO and SiO_2. Given the rejuvenation in the field we have prepared a series of MgO:SiO_2 systems impregnated with Zn(II) and Zr(IV) and screened for the conversion of EtOH to 1,3-BD.

2. Experimental Section:

2.1 Catalyst Preparation

$(MgCO_3)_4Mg(OH)_2.5H_2O$ was calcined in air at 450 °C for 16 h, ramp rate = 5 °C per minute, to form MgO. The appropriate molar ratio of MgO and SiO_2 was wet kneaded in deionised water, 30 ml for a scale of 10 g of material (the pore diameter of the SiO_2 being 60, 150 or 250 Å). This was then stirred until dryness and dried at 50 ºC. A sample of material was taken at this point and tested. Finally, $ZrO(NO_3)_2{\cdot}H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were dissolved in water (50 ml) to produce a material with 1.5 %, 0.5 % weight of Zr(IV) and Zn(II) respectively. This was stirred at 40 °C until the mixture was completely dry. Finally, the solid containing $Mg(OH)_2$:SiO_2, Zr(IV) and Zn(II) was calcined in air at 500 °C for 5 h. The metal loadings were confirmed by ICP-AES measurements.

2.2 Catalyst Testing

The catalytic tests were carried out at 325 ºC, at atmospheric pressure with a weight hourly space velocity (WHSV) of 0.3 h^{-1}. Argon was used as the carrier gas (8 ml/min), the catalyst was packed into a quartz reactor and the catalytic reactions were carried out for 3-4 h. The exhaust gases were analysed *via* GC-MS on an Agilent 7890A instrument with a HP-PLOT/Q, 30 m long 0.530 mm diameter column equipped with FID/MS detectors. The GC was calibrated as detailed elsewhere.[6] To determine the response factor (R_F) for acetone the average of the R_F's for diethyl ether and acetaldehyde were used. In all cases satisfactory carbon balances were obtained, typically better than 90%. We observed no evidence for butanols, crotonaldehyde, ethyl-acetate or acetaldol products. Presumably, crotonaldehyde and acetaldol are formed *in-situ* but are too short lived to be detected.

2.3 Characterisation

SEM was carried out on a JEOL 6480LV at 5 - 25 kV. XPS measurements were recorded using a Scienta ESCA 300 spectrometer incorporating a rotating anode Al Kα (hν = 1486.6 eV) source. BET measurements were carried out on a BELSORP Mini-II gas adsorption instrument. Samples were pre-treated at 300 °C for 420 minutes under vacuum prior to N_2 adsorption. All ^{29}Si NMR spectra were recorded at the EPSRC National Solid-state NMR service centre, Durham on a Varian VNMRS 400 MHz spectrometer and referenced to TMS, a pulse delay of 60 s was used. pXRD were recorded on a BRUKER D8-Advance diffractometer using CuKα (λ = 1.5406 Å) radiation.

3. Results and discussion:

3.1 Characterisation

The materials have been characterised by pXRD, solid-state NMR, BET surface area measurements, SEM/TEM and the metal loadings have been confirmed by ICP-AES. Materials with various molar ratios of MgO:SiO_2 [1:1{**A**}, 2:1{**B**}, 3:1{**C**}, 85:15{**D**} and 95:5{**E**}] were prepared. For the **D** series a range of different pore diameters for the SiO_2 were employed to ascertain any influence this might have on the catalysis, if any. The samples were initially characterised *via* SEM, see supporting information. The results are in-agreement with those of Kvisle.[8] The BET surface areas of various catalysts were determined and are shown in table 1. As expected there is a reduction in the specific surface area as the proportion of MgO increases in the sample. Typically, there is also a reduction in surface area going from the pure-support to the MgO:SiO_2-Zr:Zn system and is explained by the formation of ZrO_2 and ZnO particles in the pores of the catalyst.[7]

System	Surface Area (m^2g^{-1})
A	407
A_ZrZn	306
B	372
B_ZrZn	254
C	290
C_ZrZn	173
D	162
D_ZrZn	185
E_ZrZn	80

Table 1: Selected BET specific surface areas for the catalysts. The pore diameter of the silica is 60 Å.

Furthermore, samples were analysed by XPS, Table 2. As expected the supported metals are present as ZrO_2 and ZnO (with peaks at *ca*. 181 and 184 eV for the Zr $3d_{5/2}$ and $3d_{3/2}$ respectively and 1022 and 1045 eV for the Zn $2p_{3/2}$ and $2p_{1/2}$ respectively. As anticipated **D** has higher atom percentages of Mg than Si (compared to **C**).

Catalyst	O	Si	Mg	Zn	Zr
C	54.4	7.0	21.3	-	-
C_ZrZn	47.0	6.9	26.4	0.3	0.7
D	55.9	3.1	27.7	-	-
D_ZrZn	44.7	4.3	32.0	0.2	0.8
D_ZrZn_Used	44.2	4.5	33.7	0.1	0.7

Table 2. XPS data for various catalysts prepared in this study. The pore diameter for the SiO_2 is 60 Å.

The pXRD and ^{29}Si solid state MAS NMR spectra for various samples of **D** were determined, see figure 1 for the pXRD and figure 2 for ^{29}Si NMR spectra.

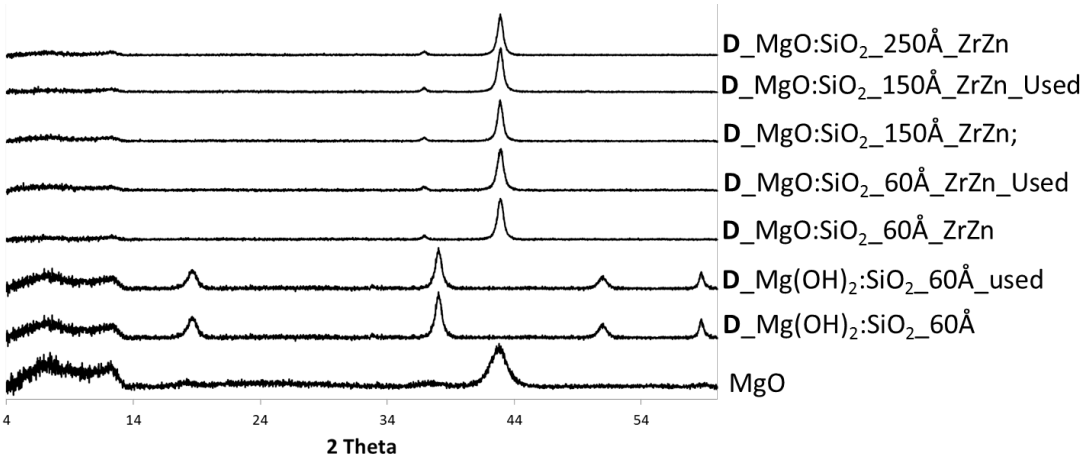

Figure 1. pXRD traces for various prepared catalysts.

In the preparation of the unsupported Mg:Si materials it is clear that the MgO transforms to $Mg(OH)_2$, with broad peaks at 2θ = 18, 38, 50 and 59 º respectively due to the rehydration of the MgO.[23] Thus, the binary Mg-Si materials in this study are truly $Mg(OH)_2$:SiO_2, even after being used in a catalysis test, figure 1. However, for the ZrZn deposited materials after calcination the pXRD clearly indicates the presence of the crystalline periclase MgO.[23] The pore diameter of the SiO_2 appears not to affect the degree of crystallinity and the pXRD of the used catalysts is analogous to that of the freshly calcined material. No peaks are observed for either ZrO_2 or ZnO phases.

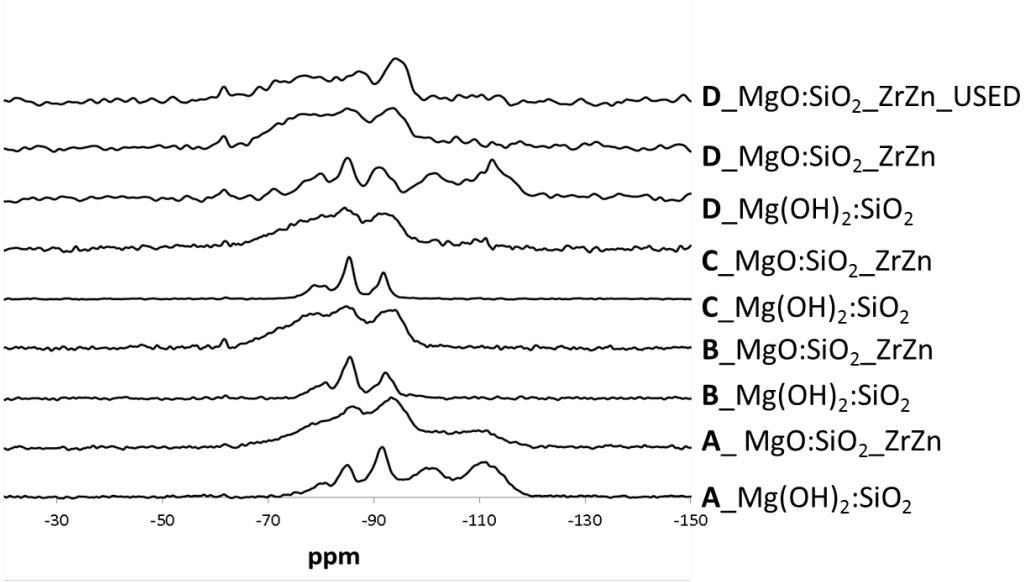

Figure 2. ^{29}Si MAS NMR spectra for various catalysts prepared in the study. The pore diameter of the SiO_2 was 60 Å in all cases.

The ^{29}Si NMR spectra have main resonances centred at -111 and -100 ppm, which are assigned as Q^4 and Q^3 silicon environments in SiO_2. There are also resonances observable at *ca.* -70, -84 and -91 ppm these are in the approximate region for Q^1, Q^2 and Q^3 sites in magnesium silicate ($MgSiO_3$) materials. Upon addition of the Zr:Zn salts and subsequent re-calcination there is a clear downfield shift in the spectra, coupled with significant broadening. This could potentially indicate that the silica phase is becoming more amorphous and indicates the formation of Mg-O-Si bonds.[23] Analysis of the catalyst before use and after use shows that they are very similar, implying no significant changes to the bulk material during catalysis.

3.2 Catalysis Testing

A WHSV of 0.3 h^{-1} was employed in all tests, a series of WHSVs were tested and this condition achieved the highest selectivity. The catalytic data for the materials is summarised in Table 3.

Catalyst	Con/%	Selectivity/%						
		C_2H_4	C_4H_8	$C_4H_{10}O$	C_2H_4O	C_4H_6	C_3H_6O	C_3H_6
A	38	57.0	2.6	30.3	1.6	7.4	0.3	1.0
B	27	34.4	6.0	12.8	2.9	39.4	1.0	3.7
C	35	34.5	4.3	10.1	2.6	43.6	1.3	3.6
D	41	46.4	1.8	18.9	4.9	26.0	0.8	1.1
A_ZrZn	51	20.6	16.2	6.2	3.5	41.1	8.0	4.4
B_ZrZn	40	14.3	12.2	1.8	7.1	48.1	13.3	3.2
C_ZrZn	35	22.3	8.5	4.1	3.5	51.3	7.0	3.4
D_ZrZn	40	15.2	6.7	6.5	5.9	62.6	0.5	2.7
E_ZrZn	30	8.7	2.6	5.9	11.1	68.7	0.9	2.1
D_ZrZn_150	33	8.1	1.8	6.2	13.2	67.7	0.6	0.7
D_ZrZn_250	10	6.3	1.5	4.8	15.5	68.5	2.4	2.7
MgO_ZrZn	5.4	29.3	1.3	0.9	46.0	18.9	1.9	1.8

Table 3: Catalytic data, WHSV = 0.3 h^{-1}, T = 325 ºC, carrier gas Ar. Conversion = $(EtOH_{in} - EtOH_{out})/EtOH_{in})$; Selectivity = $n_i/\Sigma n_i$ where n_i = number of moles of products i and Σn_i = number of moles of all products (*N.B.* H_2 and H_2O are not included in calculations). Small amounts of C_5 and C_6 hydrocarbons have been observed.

In terms of catalysts A-C there is an increase in the 1,3-BD selectivity, with significant amounts of ethene and diethyl ether also being detected. The ethene and diethyl ether are thought to be produced by acid catalysed processes (potentially catalysed by Brønsted acid sites from SiO_2) and as such their concentration reduces as the molar ratio of SiO_2 decreases. Conversely, as the amount of MgO increases then the basicity of the support increases. There has been much debate in the literature regarding the optimum ratio for MgO:SiO_2 with groups reporting different values.[8,10,14] This is the first use of a binary $Mg(OH)_2$:SiO_2 system and the results are similar to those recently reported for the more classical MgO:SiO_2 system.[8] In our case, as with MgO:SiO_2, it is presumably the $Mg(OH)_2$ that is active for the aldol condensation and dehydrogenation, whereas silica assists in the dehydration steps of the mechanism. It must be noted that there is no calcination step in the preparation of the Mg:Si only catalysts, reducing the environmental footprint of this system. These systems all show too low selectivities towards 1,3-BD to be industrially viable. It must be noted that if we calcine **D** (to generate MgO:SiO_2 85:15) we observe a slight increase in selectivity to 38 % for 1,3-BD, with ethene decreasing to 33 %, with an analogous conversion to the $Mg(OH)_2$:SiO_2 system. We have previously shown that adding ZrO_2 and ZnO to silica boosts the selectivity towards 1,3-BD.[6] We have also seen an effect of varying the pore diameter on the selectivity, for SiO_2 only systems.[6]

Interestingly, for the bi-metallic supported materials as we pass from **A** to **E** an increase in 1,3-BD selectivity is observed with a concurrent reduction in the selectivity towards ethene. It is postulated that addition of ZnO is assisting in the dehydrogenation of ethanol,[24] and ZrO_2 is assisting in the aldol condensation of the generated acetaldehyde moieties.[25] We have prepared catalyst **E**_ZrZn which only contains 5% SiO_2 on the support with only a slight improvement in selectivity compared to **D**_ZrZn, thus implying that the dehydration steps of the mechanism are facile. However, if pure MgO is used as the support then the conversion dramatically decreases (*ca.* 5 %) as does the selectivity towards 1,3-BD, indicating that a small amount of SiO_2 is essential. We have also prepared catalyst **D**_ZrZn with various pore diameters of silica (150 and 250 Å). In this case we only observed a slight increase in selectivity to 1.3-BD (*ca.* 5% going from 60 to 150 Å). This is in contrast to pure SiO_2 where a significant improvement in selectivity was observed as the pore diameter increased.[6] This may be related to the MgO attenuating any effect from the SiO_2 pore diameter. The product distribution was relatively constant over time, figure 3, for the 60 Å material. Although there was an initial decrease for the 150 Å material, such a trend has previously been observed by others.[6,7] We have calcined **D** to generate MgO:SiO_2 (85:15) and then added the metals and further calcined, to mimic previously reported mono-metallic systems.[7] Under analogous conditions a conversion of 32 % is observed with a selectivity of 68 % to 1,3-BD. Indicating, that the energy intensive calcination after generating the binary (Mg:Si) oxide, in our hands, does not offer significant advantages and is not essential in the catalyst preparation. Furthermore, TEM analysis of **D**_ZrZn {prepared from $Mg(OH)_2SiO_2$} or **D**_ZrZn {prepared from MgO:SiO_2} both have analogous amorphous irregularly shaped platelet-like morphology.

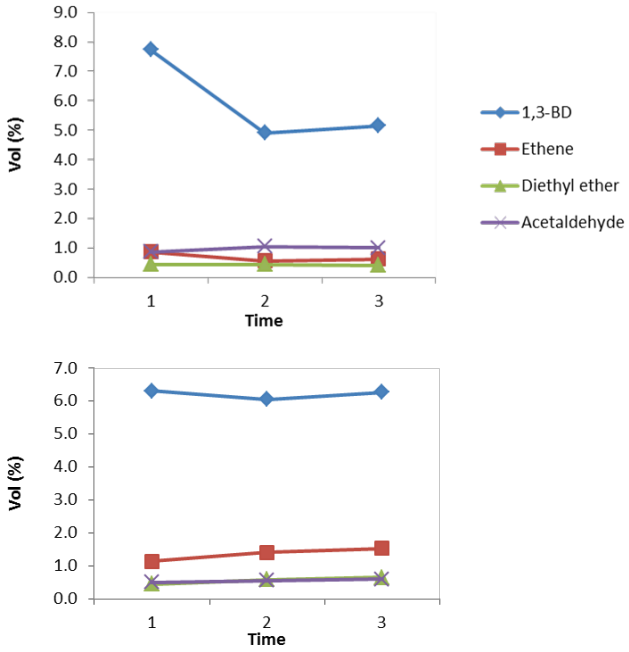

Figure 3. GC measurements of the evolution of 1,3-BD, ethene, diethyl ether and acetaldehyde for **D**_ZrZn with SiO_2 pore diameter 150 Å (upper) and 60 Å (lower).

In an attempt to probe this reaction further tests were performed with (i) CH_3CH_2OH/CD_3CD_2OD and (ii) CH_3CH_2OH/CD_3CDO, with the deuterated version present at 20 % loading (by volume). The catalyst used for the tests was **D**_ZrZn. Interestingly, the selectivity towards 1,3-BD increased to 74 % (conversion 35 %) when CD_3CDO was added to the feed. From the experiment with CH_3CH_2OH/CD_3CDO we also observed deuterium incorporation in the ethene by-product. When utilising pure H-EtOH as the feed ethene is observed with an m/z (EI mode) at 28 $gmol^{-1}$ however when H-EtOH and D-acetaldehyde (8:2) are used as the feed the maximum m/z for the ethene peak was 30 $gmol^{-1}$ indicating deuterium incorporation; such deuteration was also observed in the diethyl ether. It is generally accepted that both ethene and diethyl ether are produced *via* acid catalytic processes utilising only EtOH. Thus, the acetaldehyde must be being converted to ethanol with a deuterium content, to explain the deuterium incorporation in the ethene and diethyl ether.

4. Conclusions

A series of catalysts based on MgO:SiO_2 have been prepared, characterised and tested for the conversion of EtOH to 1,3-BD, with the highest selectivity achieved being 69 %. It was found that as the mole fraction of MgO increases then the selectivity to 1,3-BD increases, which is presumably related to MgO's ability to dehydrogenate EtOH. However, a small amount of SiO_2 is essential, as this may well aid in the dispersion of the metals and catalyse the dehydration steps in the mechanism. The addition of Zr(IV) and Zn(II) also increased the selectivity to 1,3-BD, by catalysing the aldol and dehydrogenation steps in the mechanism. To achieve the optimum conversion and selectivity to 1,3-BD the best ratio of MgO-to-SiO_2 is 95:5 with SiO_2 having a 60 Å pore diameter. Preliminary investigations with deuterated ethanol/acetaldehyde have been performed and further studies are on-going in this area.

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